




Mordenite-based catalyst for producing methylamines

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Report a data error here**Abstract of EP1077084**

Catalysts for producing methylamines are provided, which comprise mordenite, as the essential component, of spherical fine particles having a crystal diameter of not more than 0.5 μ m. When the catalysts are used for the production of dimethylamine from methanol and ammonia or through a disproportionation of methylamines, they exhibit a high dimethylamine productivity with the formation of few amount of trimethylamine whose demand is very small. Besides, the process can be operated for a long period of time without decrease in the catalyst activity.

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(54) Mordenite-based catalyst for producing methylamines

(57) Catalysts for producing methylamines are provided, which comprise mordenite, as the essential component, of spherical fine particles having a crystal diameter of not more than 0.5 μm . When the catalysts are used for the production of dimethylamine from methanol and ammonia or through a disproportionation of methylamines, they exhibit a high dimethylamine productivity with the formation of few amount of trimethylamine whose demand is very small. Besides, the process can be operated for a long period of time without decrease in the catalyst activity.

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Description**Background of the Invention****1. Field of the Invention**

[0001] The present invention relates to catalysts for producing methylamines. The catalysts have superior performances in the production of methylamines from methanol and ammonia, or through a disproportionation reaction of monomethylamine. Methylamines, including dimethylamine are used as materials for solvents such as dimethylformamide, rubber products, pharmaceuticals, surfactants, and others.

2. Description of the Prior Art

[0002] Methylamines are usually produced from methanol and ammonia in the presence of solid acid catalysts such as silica-alumina, at a temperature of approximately 400 °C. Alternatively, methylamines are produced through a disproportionation reaction of monomethylamine. The productions of methylamines as mentioned above produce mainly trimethylamine which is of little use from a commercial point of view. A selective production method of dimethylamine has long been earnestly desired, because demands for methylamines are directed to dimethylamine.

[0003] There are proposed a few methods for producing methylamines using zeolite catalysts which are more advantageous over the previous silica-alumina catalysts; for example, methods which use zeolite A (JP 56-69846 A), FU-1 (JP 54-148708 A), ZSM-5 (U.S.P. 4082805), ferrierite and erionite (JP 56-113747 A), ZK-5, Rho, chabazite and erionite (JP 61-254256 A), and silicoaluminophosphates (JP 02-734 A). They give better results than those on the basis of the thermodynamic equilibrium.

[0004] Mordenite has been investigated as a catalyst for methylamine production, among zeolite catalysts as mentioned above. U.S.P. 3384667 teaches mordenite, besides other zeolite catalysts (1968). JP 56-46846 A, JP 58-49340 A, JP 59-210050 A and JP 59-227841 A teach the use of natural or synthetic mordenites. JP 03-262540 A mentions the use of mordenite modified with silicon tetrachloride through a CVD method, in order to suppress formation of trimethylamine. There are various additional modifications by ion exchange or other methods.

[0005] Furthermore, JP 06-179640 A mentions mordenite wherein a ratio of silica to alumina is more than 10, while the ratio of silica to alumina is usually not higher than 10. JP 08-283207 A teaches rod form mordenite having aspect ratios of not less than 2, in respect to crystal form of mordenite.

[0006] There is not large difference between zeolite and silica-alumina catalysts from a commercial points of view. Zeolite catalysts are superior to silica-alumina catalysts, because the former give dimethylamine, the most desired product, with a high selectivity. However, zeolite catalysts are inferior to silica-alumina catalysts, in respect to catalyst activity. During the practical catalyst life for one year, productivity of dimethylamine is at most a half of that using the silica-alumina catalyst. Thus, even though dimethylamine is produced with a high selectivity, the advantage and disadvantage are offset when compared in the practical productivities.

[0007] The present inventors previously applied patents (JP 11-35527 A, JP Application Nos. 10-187423, 10-180879 and 10-025832), based upon the findings that silica-modified silicoaluminophosphates have a higher activity, along with a higher dimethylamine selectivity, when compared with well known zeolite catalysts and silicoaluminophosphates in the prior art. These catalysts were improved to provide a higher activity along with a higher dimethylamine selectivity, than silica-alumina catalysts, and also a superior dimethylamine productivity to that in the prior art (JP Application No. 10-293772). However, mordenites practically used as a catalyst for commercial production of methylamines are not comparable with silica-alumina catalysts, because of their lower dimethylamine productivity.

Summary of the Invention

[0008] It is an object of the invention to provide mordenite catalysts for producing methylamines, which facilitate the producing process, by improving low productivity encountered by the previous mordenite catalysts, i.e., increasing dimethylamine yield per catalyst amount (STY) up to the same as or higher than that in the conventional silica-alumina catalysts, together with high dimethylamine selectivity.

[0009] The present inventors have found that mordenites of nearly spherical crystal having an aspect ratio of not higher than 2 exhibit excellent catalytic performance, against previous teachings that such mordenite is not suitable as the catalysts for production of methylamine (JP 08-283207 A). Furthermore, they have also found that mordenites containing particular elements exhibit a high dimethylamine selectivity and have a practical catalyst life with small decrease in activity along the passage of time. In addition, they are superior to silica-alumina catalysts with respect to dimethylamine STYs and productivity. Thus, the present invention has been accomplished on the basis that both a large productivity and a high dimethylamine selectivity are given to catalysts for methylamines.

[0010] The present invention relates to

- (1) a catalyst for producing methylamines, which comprises, as the essential component, mordenite of spherical fine particles having a crystal (single crystal) diameter of not more than 0.5 μm ;
- (2) a catalyst according to the item (1), in which the mordenite contains at least one element selected from the group consisting of Li, Be, Mg, La, Ce, Ca, Sr, Th, Y, Ti, Zr, V, Nb, Ta, Cr, Mn, Fe, Ru, Co, Rh, Ir, Ni, Pd, Pt, Cu, Zn, B, Ga, In, Ge and Sn;
- (3) a catalyst according to the item (1), in which the mordenite contains at least one element selected from the group consisting of Ti, Y, Zr, Nb, Ta, Ga, In, Zn, Ge and Sn;
- (4) a method for producing methylamines through a reaction of ammonia and methanol in the presence of the catalyst for producing methylamines according to any of the items (1) to (3) mentioned above; and
- (5) a method for producing methylamines, which comprises conducting a disproportionation reaction of monomethylamine in the presence of the catalyst for producing methylamines according to any of the items (1) to (3) mentioned above.

Brief Description of Drawing

[0011]

Fig. 1 is a transmission electron microscope image of a catalyst 1 mentioned in Example 1 below.

Description of the Preferred Embodiments

[0012] Mordenites according to the present invention may be natural or synthetic ones. It may be of spherical or nearly spherical, for example, ellipsoidal form crystals. The crystal diameter is not more than 0.5 μm . The aspect ratio of such crystals corresponds to not more than 2, i.e., the crystal has almost the same sizes in the longitude and latitude. The aspect ratio of mordenites is represented by an axis ratio of c/b or c/a , wherein the axis c is that along the front view direction of the 12-membered ring micropore, and the axis b is that along the front view direction of the 8-membered ring side surface, with the axis a being the remainder. When mordenite is of spherical fine particles having a crystal diameter of not more than 0.5 μm , it is hardly detected by an electron microscope of a low magnification. Crystal size can be observed using a scanning or transmission electron microscope of 20 to 1,000 thousand magnifications. Preferable crystal diameter is from 0.05 to 0.1 μm . There is no particular limitation to the form and size of the secondary particles, i.e. aggregated crystals. The mordenites have a satisfactory catalytic life, so far as the crystal has a suitable form and size as mentioned above.

[0013] Preferably, the Si/Al ratio of the mordenites is from 5 to 10. Although this range is not limitative, too large Si/Al ratios, for example, as large as 100, result in unfavorable decrease in the conversion ratio. As for the activity, H-type mordenites are superior to Na-type ones. An amount of Na as impurity is preferably as small as possible, but an amount of not more than 2000 ppm causes no problem from a practical view point. An amount of alkali metals other than Na is preferably not more than 2000 ppm.

[0014] In order to improve the activity and selectivity, the mordenite is preferably calcined to form the H-type, after the Na or other alkali metals are exchanged with ammonium ions. Furthermore, it may preferably be modified with other suitable ions, such as Li, Be, Mg, La, Ce, Ca, Sr, Th, Y, Ti, Zr, V, Nb, Ta, Cr, Mn, Fe, Ru, Co, Rh, Ir, Ni, Pd, Pt, Cu, Zn, B, Ga, In, Ge and Sn. The ion exchange modification may be carried out by any means, for example, by immersing the mordenites in an ion solution, followed by washing with water, drying and calcination. The degree of ion exchange is preferably at least 10%, more preferably not less than 30% of the ion exchangeable capacity in mordenites.

[0015] Other methods to improve the activity and selectivity of the present mordenites include a modification by exchanging a part of the components with adequate elements through other methods than the immersion, or by coating or sedimenting adequate elements onto the mordenites. Such elements involve metals, submetals and semiconductors, including Li, Be, Mg, La, Ce, Ca, Sr, Th, Y, Ti, Nb, Ta, Zr, V, Cr, Mn, Fe, Ru, Co, Rh, Ir, Ni, Pd, Pt, Cu, Zn, B, Ga, In, Ge and Sn. Particularly, Ti, Y, Zr, Nb, Ta, Ga, In, Ge and Sn are preferred.

[0016] These elements mentioned above for modification may be contained in the mordenites in the form of simple substance atoms, oxides or double oxides. Since the mordenites are usually calcined before the catalytic usage, they are mostly present in the form of oxides, such as lithium oxide, beryllium oxide, lanthanum oxide, calcium oxide, strontium oxide, yttrium oxide, titanium oxide, niobium oxide, tantalum oxide, zirconium oxide, vanadium oxide, chromium oxide, manganese oxide, iron oxide, ruthenium oxide, cobalt oxide, rhodium oxide, iridium oxide, nickel oxide, palladium oxide, zinc oxide, copper oxide, boron oxide, gallium oxide, indium oxide, germanium oxide and tin oxide. The preferable content of the elements above in the mordenites is not more than 50% by weight, calculated as an oxide of the element, on the basis of mordenites, preferably within the range from 0.5 to 10% by weight.

[0017] The other modes for the modification are a method in which elements are mixed mechanically with mordenites, a method in which the elements are added during the course of hydrothermal synthesis, a method according to chemical vapor deposition (CVD), or a method of thermal cracking after the contact with precursors. Among them, the mechanical mixing of the oxides, or the addition of the metallic sources during the hydrothermal synthesis are particularly preferable, from view points of simplicity and steadiness.

[0018] The modification or alteration methods as described above are not critical. Any mordenites containing particular metals or oxides thereof as a part of the components fall within the scope of the invention, as long as they are prepared by exchanging, binding, sedimentation, coating, or any other process.

[0019] Mordenites are one of crystalline aluminosilicates zeolites. Zeolites such as ferrierite, epistilbite or ZSM-5 are considered to be in a series of mordenites. The zeolites have the same specific structural arrangement as mordenites, namely with respect to the secondary building units composed of the primary building unit of AlO_4 and SiO_4 tetrahedrons in the frameworks ("Science and Application of Zeolite", by KODANSHA Scientific). Furthermore, the regions of compositions from which crystals are formed are close each other. In the present invention, such zeolites may be used in place of the mordenites.

[0020] Synthetic mordenites used as the catalyst for producing methylamines according to the present invention may be prepared by any known methods from aluminum sources, such as aluminum sulfate, and silicon sources such as water glass. Among the mordenite catalysts for producing methylamines according to the present invention, unmodified ones are commercially available. One of examples of such mordenites is HSZ-630 HOA manufactured by TOSO KABUSHIKI KAISHA. Such commercially available mordenites can also be modified according to any method as mentioned above.

[0021] The present mordenite catalyst may be mixed with inexpensive, easily available or any suitable molecular sieves, for example, aluminosilicates or silicoaluminophosphates (SAPO) having micropore diameters of not more than 1 nm, such as chabazite, erionite, ferrierite, epistilbite, clinoptilolite, paulingite, phillipsite, levynite, zeolite-A, rho, ZK-5 and FU-1.

[0022] The present catalyst may contain, as binders, clay minerals such as kaolinite, halloysite, nacrite, montmorillonite, illite and mica. When mixed, the mordenite content in the mixtures is preferably not less than 50% by weight. The mordenite catalysts may be used as they are, or in the forms of tablets. Alternatively, compression or extrusion shaping may be applied to. They are used for a reaction of ammonia and methanol or dimethyl ether, a reaction of monomethylamine and methanol, or a conversion reaction through disproportionation of monomethylamine to dimethylamine.

[0023] These reactions mentioned above may be carried out in a gas phase fixed bed or fluidized bed, or in other flowing systems with or without nitrogen or hydrogen gas.

[0024] The production of methylamines or disproportionation reaction of monomethylamine using the catalyst according to the invention is carried out at a temperature preferably within the range from 200 to 400 °C, more preferably from 250 to 350 °C. The mol ratio of ammonia to methanol, N/C, in the feeding materials, is most preferably within the range from 0.5 to 2. The materials are preferably fed at a space velocity (GHSV) of 200 to 5000 h^{-1} . The reaction may be conducted under any pressure, namely under reduced pressure or under pressure. Preferably, it may be within the range from 0.1 to 10 MPa. The above embodiments of the present invention are not limitative.

[0025] Hereinafter, the present invention will more fully be described in reference to Examples and Comparative Examples, wherein the reaction were conducted using a flowing reaction apparatus which provides a material tank, feeding pumps, inlets for inert gas, reaction tubes (inner diameter of 13 ϕ , length of 300mm, SUS 316L), a sampling tank, back pressure valves, etc. A product sample was taken over one hour, after the reaction reached the stationary state, and analyzed using a gas chromatography to measure the distribution of the product composition.

Example 1

[0026] Material mordenite having an Si/Al ratio of 8 (HSZ-630 HOA, manufactured by TOSO KABUSHIKI KAISHA) was found to be of spherical fine particles having a crystal diameter of not more than 0.1 μm , from the observation of a transmission electron microscope (TEM) image (Figure 1). The mordenite was shaped by compression, then pulverized and sieved to obtain a 1 to 2 mm particle size product, as Catalyst 1.

[0027] Into the reaction tube was filled 4.5 g (10 ml) of Catalyst 1. A mixture of methanol and ammonia in 1 : 1 weight ratio was supplied thereto at a rate of 15 g per hour and 2500 h^{-1} GHSV, and a reaction was conducted under 2 MPa pressure at a temperature of 320 °C. The results of the reaction after 6 hours from the start of flowing are as follows:

Methanol conversion:	99.2%
Selectivity:	
monomethylamine	32% by weight
dimethylamine	52% by weight
trimethylamine	16% by weight

Example 2

[0028] The mordenite used in Example 1 was mixed with 5% by weight of zirconium oxide in water, and the mixture was well agitated. The mixture was dried at 110 °C overnight, and then calcined at a temperature of 600 °C for 4 hours. The resulting powder was shaped by compression, pulverized and then fractionated by sieving to obtain a 1 to 2 mm size product, as catalyst 2. The results of the reaction under the same conditions as in Example 1 are as follows:

Methanol conversion:	99.2%
Selectivity:	
monomethylamine	33% by weight
dimethylamine	62% by weight
trimethylamine	5% by weight

Comparative Example 1

[0029] A catalyst was prepared and used for a reaction in a similar way as in Example 1, except that material mordenite in the hexagonal plate form having an Si/Al ratio of 7.5 and a crystal diameter of 1.0-3.0 µm x 5.5 µm with an aspect ratio of not less than 2 (HSZ-620 HOA, manufactured by TOSO KABUSHIKI KAISHA) was used. Also, the catalyst was modified with zirconium oxide in a similar way as in Example 2. The results are shown in Table 1.

Comparative Example 2

[0030] A catalyst was prepared and used for a reaction in a similar way as in Example 1, except that material mordenite of rod form crystals having an Si/Al ratio of 9.5 and a crystal diameter of 0.1-1.3 µm x 0.5 µm with an aspect ratio of 2 to 5 (HSZ-640 HOA, manufactured by TOSO KABUSHIKI KAISHA) was used. Also, the catalyst was modified with zirconium oxide in a similar way as in Example 2. The results are shown in Table 1.

Comparative Example 3

[0031] A catalyst was prepared and used for a reaction in a similar way as in Example 1, except that material mordenite of ellipsoidal crystals having an Si/Al ratio of 9 and a crystal diameter of 0.5 µm x 1.0 µm with an aspect ratio of about 1 to 2 (LZM-8, manufactured by UOP) was used. Also, the catalyst was modified with zirconium oxide in a similar way as in Example 2. The results are shown in Table 1.

Comparative Example 4

[0032] A catalyst was prepared and used for a reaction in a similar way as in Example 1, except that material mordenite of rod form and spherical crystals having an Si/Al ratio is 101 and a crystal diameter of 0.6-1.4 µm x 0.6 µm with an aspect ratio of not less than 2 (HSZ-690 HOA, manufactured by TOSO KABUSHIKI KAISHA) was used. Also, the catalyst was modified with zirconium oxide in a similar way as in Example 2. The results are shown in Table 1.

Comparative Example 5

[0033] A catalyst was prepared and used for a reaction in a similar way as in Example 1, except that natural mordenite having an Si/Al ratio of 9.5 and an indistinguishable crystal diameter with an aspect ratio of not less than 2, as a mixture of fibrous and rod-form crystals (#1424, manufactured by SHIN-TOHOKU KAGAKU KOGYO KABUSHI KAI-SHA) was used. The results are shown in Table 1.

[0034] Examples 1 and 2 and Comparative Examples 1 through 5 show that mordenite of nearly spherical fine particles having not more than 0.5 μm crystal size exhibits excellent selectivity and activity when used as it is, or after modification with an oxide. On the other side, mordenite of plate or rod form exhibits insufficient selectivity when used singly or after modification with an oxide, and is not suitable as a catalyst for producing methylamines. It has now been found that mordenite of spherical fine particles, which has heretofore been considered not to be suitable for the reaction, rather exhibits excellent performance for the reaction.

Examples 3 to 22

[0035] Catalysts were prepared in a similar way as in Example 2, except that, in place of the zirconium oxide modifier, an oxide of Si, La, Ce, Mg, Ba, Sr, Th, Y, Ti, Nb, Mn, Fe, Co, Ni, Pd, Cu, Zn, In or Sn, respectively, or kaolinite which is a typical clay mineral, is used as the respective modifier.

[0036] Into the reaction tube was filled 4.5 g (10 ml) of each catalyst. A mixture of methanol and ammonia in 1 : 1 weight ratio was supplied thereto at a space velocity (GHSV) of 1500 h^{-1} , and a reaction was conducted under 2 MPa pressure at a temperature of 300 °C. The results of the reactions after 6 hours from the start of flowing are shown collectively in Table 2.

Example 23

[0037] An aqueous sulfuric acid solution of aluminum sulfate and an aqueous water glass solution were added dropwise into an aqueous sodium chloride solution under stirring. Zirconium oxide was added thereto in such an amount as to form 5 % by weight in the catalyst, and a hydrothermal synthesis was conducted at a temperature of 180 to 190 °C for 24 hours. The resulting mordenite was of nearly spherical form and had a crystal diameter of 0.1 μm with an aspect ratio of 1 to 2.

[0038] A mixture of methanol and ammonia in 1 : 1 weight ratio was supplied at a space velocity (GHSV) of 1500 h^{-1} , and the reaction was conducted at a temperature of 300 °C under 2 MPa pressure. The results of the reaction after 6 hours from the start of flowing are shown in Table 2.

Example 24

[0039] Mordenite used in Example 1 was immersed in a copper formate dispersion in butanol (10% by weight), then taken out of the dispersion and dried. The mordenite was heated to 220 °C under 1 mmHg subatmospheric pressure for thermal decomposition of the copper formate (a kind of CVD method), thereby the copper being sedimented onto the mordenite. A catalyst was prepared in a similar way as in Example 1 and used for a reaction.

[0040] The reaction was conducted at a GHSV of 2500 h^{-1} under 2 MPa pressure at a temperature of 320 °C. The results of the reaction after 6 hours from the start of flowing are as follows:

Methanol conversion:	98.2%
Selectivity:	
monomethylamine	32% by weight
dimethylamine	60% by weight
trimethylamine	8% by weight

Example 25

[0041] A synthesized H-type ZSM-5 (Si/Al ratio of 10) catalyst containing 5% by weight of zirconium oxide was prepared in a similar way as in Example 2.

[0042] A mixture of methanol and ammonia in 1 : 1 weight ratio was supplied at a space velocity (GHSV) of 1500 h⁻¹ and a reaction was conducted under 2 MPa pressure at a temperature of 300 °C. The results of the reaction after 6 hours from the start of flowing are shown in Table 2.

5 Example 26

[0043] Using a catalyst containing 5% by weight of kaolinite, prepared in a similar way as in Example 2, monomethylamine was supplied at a GHSV of 700 h⁻¹, and a disproportionation reaction of monomethylamine was conducted at a temperature of 300 °C under 2 MPa pressure to form ammonia and dimethylamine, with the results as shown in Table 3.

Example 27 A disproportionation reaction of monomethylamine was

[0044] conducted in a similar way as in Example 26, except that a catalyst containing 5% by weight of zirconium oxide was used, in place of the kaolinite, with the results of the reaction as shown in Table 3.

Example 28

[0045] Using catalyst 2 prepared from material mordenite of spherical fine particles having an Si/Al ratio of 8 and a crystal diameter of not more than 0.1 µm (HSZ-630 HOA, manufactured by TOSO KABUSHIKI KAISHA), a mixture of methanol and ammonia in 1 : 1 weight ratio was supplied at a space velocity (GHSV) of 1500 h⁻¹, and the reaction was continued under 2 MPa pressure at a temperature of 320 °C.

[0046] After 3000 hour reaction, the methanol conversion ratio remained at 95% or more. The dimethylamine production rate at this time was 0.36 kg/L-cat.h, and no change was observed in the amine selectivity.

Comparative Example 6

[0047] Using a catalyst from hexagonal plate mordenite having an Si/Al ratio of 7.5 and a crystal diameter of 1.0-3.0 µm x 5.5 µm with an aspect ratio of not less than 2 (HSZ-620 HOA, manufactured by TOSO KABUSHIKI KAISHA), a mixture of methanol and ammonia in 1 : 1 weight ratio was supplied at a space velocity (GHSV) of 1500 h⁻¹, and a reaction was conducted under 2 MPa pressure at 320 °C, with the results as shown in Table 4.

Comparative Example 7

[0048] A reaction was conducted in a similar way as in Comparative Example 6, except that a catalyst from rod-form mordenite having an Si/Al ratio of 9.5 and a crystal diameter of 0.1-1.3 µm x 0.5 µm with an aspect ratio of 2 to 5 (HSZ-640 HOA, manufactured by TOSO KABUSHIKI KAISHA) was used, with the results as shown in Table 4.

Comparative Example 8

[0049] A reaction was conducted in a similar way as in Comparative Example 6, except that a catalyst from mordenite of spherical crystals having an Si/Al ratio of 9 and a crystal diameter of 0.5 µm x 1.0 µm with an aspect ratio of 1 to 2 (LZM-8, manufactured by UOP) was used, with the results as shown in Table 4.

Comparative Example 9

[0050] A reaction was conducted in a similar way as in Comparative Example 6, except that a catalyst from natural mordenite composed of mixed fibrous and rod-form crystals having an Si/Al ratio of 9.5 and an indistinguishable crystalline diameter with an aspect ratio of not less than 2 (#1424, manufactured by SHIN-TOHOKU KAGAKU KOGYO KABUSHIKI KAISHA) was used, with the results as shown in Table 4.

Comparative Example 10

[0051] Using an amorphous silica-alumina catalyst, a mixture of methanol and ammonia in 1 : 1 weight ratio was supplied at a space velocity (GHSV) of 1500 h⁻¹, and a reaction was continued under 2 MPa pressure at a temperature of 400 °C. After 3000 hour reaction, the methanol conversion ratio was 99.2%. After 8000 hours, the ratio was 97.2%. Assuming that the practical life is one year or longer, the dimethylamine production rate was 0.21 kg/L-cat.h or more. The amine selectivity remained as mono-, di- and trimethylamine of 24, 25 and 51 % by weight, respectively, through

the testing period.

[0052] Examples and Comparative Examples mentioned above show that the catalysts according to the present invention exhibit a high dimethylamine productivity with few amount of trimethylamine, of which the demand is less, in the dimethylamine production process from methanol and ammonia or through a disproportionation reaction of methylamines. Besides, the process can be operated for longer period of time without decrease in the catalyst activity.

Table 1

Properties of catalysts and the results (after 6 hrs from the start of flowing)									
Examples	Catalysts	Si/Al	Crystal diameter μm	Forms	Aspect ratio	Conversion methanol (%)	Amine selectivity (wt.%)		
							m	d	t
Ex.1	mordenite (Catalyst 1)	8	0.05-0.1	sphere	1-2	99.2	32	52	16
Ex.2	mordenite (Catalyst2)	8	0.05-0.1	sphere	1-2	99.2	33	62	5
Comp. Ex.1	mordenite	7.5	1.0-3.0x5.5	hexagonal plate	>2	99.1	23	25	52
	Zr-modified mordenite					98.9	22	25	53
Comp. Ex.2	mordenite	9.5	0.1-1.3x0.5	rod	2-5	99.4	22	25	54
	Zr-modified mordenite					99.2	22	25	53
Comp. Ex.3	mordenite	9	0.5-1.0	sphere	1-2	99.2	22	25	53
	Zr-modified mordenite					98.8	23	24	53
Comp. Ex.4	mordenite	101	0.6-1.4x0.6	rod-sphere	>2	39.0	36	32	33
	Zr-modified mordenite					37.5	32	42	26
Comp. Ex.5	natural mordenite	9.5		fiber-rod	>2	38.0	69	28	3
Reaction conditions: temp. 320 °C, pressure 2 MPa, and GHSV 2500 h ⁻¹ In the amine selectivity, m: monomethylamine d: dimethylamine t: trimethylamine									

Table 2

Results from modified mordenites (reaction of methanol and ammonia)								
		Molecular sieves	Modifiers	Amount added (wt.%)	Methanol conversion ratio(%)	Amine selectivity (wt.%)		
						m	d	t
5	Ex. 3	mordenite	silica poweder	5	98.6	32	56	12
10	Ex. 4	mordenite	lanthanum oxide	5	95.5	33	60	7
15	Ex. 5	mordenite	cerium oxide	5	94.4	33	60	7
	Ex. 6	mordenite	magnesium oxide	5	86.1	33	59	8
	Ex. 7	mordenite	barium oxide	5	92.1	36	57	7
20	Ex. 8	mordenite	strontium oxide	5	93.8	33	62	5
	Ex. 9	mordenite	thorium oxide	5	93.1	33	60	7
	Ex.10	mordenite	yttrium oxide	5	93.5	35	60	5
25	Ex.11	mordenite	titanium oxide	5	98.0	35	61	4
	Ex.12	mordenite	niobium oxide	5	96.0	33	60	7
30	Ex.13	mordenite	manganese oxide	5	97.0	32	59	9
	Ex.14	mordenite	iron oxide	5	98.1	36	59	5
35	Ex.15	mordenite	cobalt oxide	5	94.1	32	59	9
	Ex.16	mordenite	nickel oxide	5	96.6	33	60	7
	Ex.17	mordenite	palladium oxide	5	97.0	33	61	6
40	Ex.18	mordenite	copper(I) oxide	5	95.1	32	58	10
	Ex.19	mordenite	zinc oxide	5	78.1	40	58	2
	Ex.20	mordenite	indium oxide	5	96.6	32	62	6
45	Ex.21	mordenite	tin(IV) oxide	5	96.2	32	61	7
	Ex.22	mordenite	kaolinite	5	97.6	35	60	5
	Ex.23	mordenite	zirconium oxide	5	97.4	33	59	8
50	Ex.25	ZMS-5	silica powder	5	97.6	29	38	33

Table 2 (continued)

Results from modified mordenites (reaction of methanol and ammonia)							
	Molecular sieves	Modifiers	Amount added (wt.%)	Methanol conversion ratio(%)	Amine selectivity (wt.%)		
					m	d	t
Comp. Ex.10	silica-alumina	zirconium oxide		99.6	24	25	51
Reaction conditions: temp. 300 °C (Comp. Ex. 10, 400 °C), pressure 2 MPa, and GHSV 1500 hr ⁻¹ Mordenite: HSZ630 HOA (manufactured by TOSO K.K.) In the amine selectivity, m: monomethylamine d: dimethylamine t: trimethylamine							

Table 3

Results from modified mordenites (disproportionation reaction of monomethylamine)						
	Molecular sieves	Modifiers	Amount added (wt.%)	Monomethylamine conversion (%)	Amine selectivity	
					d	t
Ex. 26	mordenite	kaolinite	5	82.6	88	12
Ex. 27	mordenite	zirconium oxide	5	80.5	91	9
Reaction conditions: Temp. 300°C, pressure 2 MPa, and GHSV 700 hr ⁻¹ Mordenite: HSZ630 HOA (from TOSO K.K.) In the amine selectivity, d: dimethylamine t: trimethylamine						

Table 4

Catalyst activity and dimethylamine productivity							
Examples	Catalysts	Crystal diameter μm	Forms	Methanol conversion ratio (%)			Dimethylamine selectivity STY Kg/L-cat.h
				6h	1500h	3000h	
Ex.28	Catalyst 2	0.05-0.1	sphere	98.9	97.4	95.8	0.36
Comp. Ex. 6	mordenite (HSZ-620 HOA)	1.0-3.0x5.5	hexagonal plate	99.1	94.8	90.2	0.13
Comp. Ex. 7	mordenite (HSZ-640 HOA)	0.1-1.3x0.5	rod	99.4	95.4	92.4	0.14

Table 4 (continued)

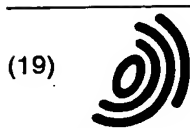
Catalyst activity and dimethylamine productivity							
Examples	Catalysts	Crystal diameter μm	Forms	Methanol conversion ratio (%)			Dimethylamine selectivity STY Kg/L-cat.h
				6h	1500h	3000h	
Comp. Ex. 8	mordenite (UOP LZM-8)	0.5x1.0	sphere	99.2	96.2	94.1	0.15
Comp. Ex. 9	mordenite (SHIN-TOHOKU K.K.)	(unknown)	fiber-rod	47.2	-	-	0.05
Comp. Ex.10	silica-alumina			99.6	99.4	99.2	0.21
Reaction conditions: temp. 320 °C (Comp. Ex. 10, 400 °C), pressure 2 MPa, and GHSV 1500 hr ⁻¹							

Claims

1. A catalyst for producing methylamines, which comprises, as the essential component, mordenite of spherical fine particles having a crystal diameter of not larger than 0.5 μm .
2. A catalyst according to Claim 1, in which the mordenite contains at least one element selected from the group consisting of Li, Be, Mg, La, Ce, Ca, Sr, Th, Y, Ti, Zr, V, Nb, Ta, Cr, Mn, Fe, Ru, Co, Rh, Ir, Ni, Pd, Pt, Cu, Zn, B, Ga, In, Ge and Sn.
3. A catalyst according to Claim 1, in which the mordenite contains at least one element selected from the group consisting of Ti, Y, Zr, Nb, Ta, Ga, In, Zn, Ge and Sn.
4. A method for producing methylamines, which comprises allowing ammonia to react with methanol in the presence of a catalyst for producing methylamines according to any of Claims 1 to 3.
5. A method for producing methylamines, which comprises conducting a disproportionation reaction of monomethylamine in the presence of a catalyst for producing methylamines according to any of Claims 1 to 3.

FIG. 1





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(54) **Mordenite-based catalyst for producing methylamines**

(57) Catalysts for producing methylamines are provided, which comprise mordenite, as the essential component, of spherical fine particles having a crystal diameter of not more than 0.5 μm . When the catalysts are used for the production of dimethylamine from methanol and ammonia or through a disproportionation of meth-

ylamines, they exhibit a high dimethylamine productivity with the formation of few amount of trimethylamine whose demand is very small. Besides, the process can be operated for a long period of time without decrease in the catalyst activity.

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DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
P,X	EP 0 967 011 A (MITSUBISHI GAS CHEMICAL CO) 29 December 1999 (1999-12-29) * claims; examples 6-24 *	1-5	B01J29/18 C07C209/16 B01J29/20 B01J29/22
X	EP 0 681 869 A (MITSUI TOATSU CHEMICALS) 15 November 1995 (1995-11-15) * example 1 *	1,4,5	
X	US 4 588 846 A (MITSUI OSAMU ET AL) 13 May 1986 (1986-05-13) * column 6, line 43 - column 7, line 8; claims 2,7-10; examples * * column 8, line 51-56 *	1-3	
X	EP 0 816 311 A (TORAY INDUSTRIES) 7 January 1998 (1998-01-07) * page 5, line 1 - page 6, line 7 *	1,2	
X	PATENT ABSTRACTS OF JAPAN vol. 1999, no. 05, 31 May 1999 (1999-05-31) & JP 11 028363 A (TORAY IND INC), 2 February 1999 (1999-02-02) * abstract *	1,2	
			TECHNICAL FIELDS SEARCHED (Int.Cl.7)
			B01J C07C
The present search report has been drawn up for all claims			
Place of search MUNICH		Date of completion of the search 22 January 2002	Examiner Schwallier, J-M
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EPO FORM 1503 03.82 (P/M/C01)

**ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.**

EP 00 11 5542

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on
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22-01-2002

Patent document cited in search report		Publication date		Patent family member(s)	Publication date
EP 0967011	A	29-12-1999	JP	2000005604 A	11-01-2000
			EP	0967011 A2	29-12-1999
			US	6180828 B1	30-01-2001
EP 0681869	A	15-11-1995	CN	1114308 A ,B	03-01-1996
			EP	0681869 A1	15-11-1995
			JP	8283207 A	29-10-1996
			KR	157704 B1	01-12-1998
			US	5959150 A	28-09-1999
US 4588846	A	13-05-1986	JP	1742434 C	15-03-1993
			JP	2031056 B	11-07-1990
			JP	60104028 A	08-06-1985
			JP	1001453 B	11-01-1989
			JP	1698108 C	28-09-1992
			JP	60104030 A	08-06-1985
			DE	3441072 A1	23-05-1985
			GB	2151224 A ,B	17-07-1985
			FR	2554440 A1	10-05-1985
EP 0816311	A	07-01-1998	JP	10045640 A	17-02-1998
			CA	2209065 A1	28-12-1997
			DE	69708520 D1	10-01-2002
			EP	0816311 A1	07-01-1998
			JP	10071334 A	17-03-1998
			SG	67397 A1	21-09-1999
			TW	380057 B	21-01-2000
			US	6060417 A	09-05-2000
JP 11028363	A	02-02-1999	EP	0940177 A2	08-09-1999
			SG	74639 A1	22-08-2000

EPO FORM P0459

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82